October 1, 1968

(U) IGNITION RESPONSE OF SOLID PROPELLANTS TO RADIATION AND CONDUCTION*†

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ABSTRACT

Experimental measurements were carried out on the ignition response of solid propellants to radiative and to conductive heat transfer. The propellants were composed of ammonium perchlorate and different organic binders. The experimental results were interpreted in terms of a model involving exothermic chemical reaction in the condensed phase of the propellant. The heat release rates in the surface-coupled reactions were measured independently. Such a model adequately fitted the ignition process associated with a thermal runaway in the condensed phase. A comparison of the ignition data demonstrated different response of the propellants to the mode of ignition. The importance of these results to rocket motor tests is discussed.

I. INTRODUCTION

The problem of solid-propellant igntion has received considerable study in recent years because of its importance to rocket technology.[1,2] The studies have been concerned with evaluations of such parameters as igntion energy and ignition time as a function of the chemical and physical properties of the propellant and the gaseous environment. In the evaluation of propellant ignitability a number of techniques have been employed that utilize various forms of energy sources and modes of energy transfer. The experimental results derived from such experiments have been interpreted on the basis of models emphasizing to various degrees the contribution of gas-phase, condensed-phase, and surface reactions. It remains to be examined whether the different ignition stimuli cause variations in ignition response and whether the ignition results obtained can be related to actual rocket motor ignition tests.[3]

In a preceding publication[4] the contribution of exothermic heterogeneous reactions to the ignition of a propellant was examined. The propellant was composed of ammonium perchlorate (AP) and copper-chromite catalyst, and Radiation from an arc-image furnace was employed as an energy source. The ignition results were interpretable in terms of a thermal runaway triggered by exothermic heterogeneous reactions in the propellant. It appeared desirable to extend these measurements to solid propellants containing organic binder. In addition, it was of interest to explore the role of the ignition mode by exposure of the same propellants to radiant or conductive energy during the preignition period.

II. EXPERIMENTAL DETAILS

Materials

The propellants employed in our studies were composed of ammonium perchlorate and organic binder. Their compositions are shown in Table I. Propellants A and B were cured at 80°C for 3 days, while propellant C was cured at 80°C for 4 days. The propellants were stored in a desiccator

(over $CaCl_2$) for various lengths of time before use in the ignition experiments.

Energy Sources

The arc-image furnace used as a source of igntion energy in the experiments described in this paper was identical to that previously employed.[5] Calibration of the incident radiant flux was carried out preceding the experimental measurements. No correction was made for reflectance or transmittance because of the opacity of the samples employed. In the radiation-ignition studies propellant B was used (Table I). This propellant was identical to propellant A except for a small amount of magnetite which was added primarily as an absorber for the incident radiation. The catalytic properties of the magnetite in the condensed phase were found to be negligible under our experimental conditions.

For ignition by conductive heat transfer a niobium ribbon (width 0.915 mm, thickness 0.056 mm, length 28.6 mm)* was employed. A rectangular piece of propellant under study (28.6 x 7 x 6.4 mm) was cut in the center, along the long axis, and the ribbon was placed between the two sections in a "sandwich-like" fashion. The entire assembly was placed in a pressure vessel made of stainless steel and provided with electrical lead-ins, pressure fittings, and valves. Nitrogen gas at the desired total pressure was introduced into the pressure vessel before each ignition experiment.

Niobium was used because of its high temperature coefficient of resistivity, high melting point, and relatively low rate of oxidation. Although the catalytic properties of niobium are not known, one would not expect unusual catalytic activity under our experimental conditions.

*From United Mineral and Chemical Corp., Purity of Nb-metal ribbon 99.8 wt %.

A special electrical circuit was designed to rapidly raise the temperature of the ribbon to a predetermined temperature (preset average electrical resistance) and to maintain this temperature until ignition occurred.[6] The response characteristics of the electrical heating circuit were found to yield a constant ribbon temperature in less than 0.025 sec after turning on the electrical power supply (12 V storage battery). The ends of the niobium ribbon leading from the propellant were clamped to heavy aluminum electrodes which were spring loaded to keep some tension on the ribbon during the heating process. During the experiments the voltage and current were recorded on an Offner RS Dynagraph recorder* or on an oscilloscope. Ignition of the propellant was associated with an abrupt change in the voltage-current characteristics of the ribbon or an open circuit due to a burnt-out ribbon.

The average temperature of the ribbon under steady-state conditions could be calculated from the room-temperature resistance and the temperature coefficient of resistivity of niobium. However, because of conductive heat loss from the ends of the ribbon a temperature gradient prevailed along the ribbon. Consequently, a series of measurements was carried out to ascertain the maximum temperature of the ribbon (in the central position) for a specified electrical power input. This was done by heating the entire assembly in an atmosphere of helium and measuring the temperature at the center of the ribbon with an Infrascope radiation thermometer.** Helium was employed because its thermal conductivity is of the same magnitude as that of the propellant.

III. ANALYSIS OF EXPERIMENTAL RESULTS

The immediate objectives of our studies were: (a) to examine the role of exothermic surface-coupled reactions in ignition, and (b) to

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*Beckman Instruments, Inc.

**Huggins Laboratories, Inc., Sunnyvale, California

compare the response of the same propellants to ignition by radiative and conductive heat transfer. These two ignition modes exhibit basic differences in the way in which the energy is transferred to the propellant surface. In radiative ignition the energy flux to the surface remains constant while the surface temperature rises to a critical value associated with ignition. In conductive ignition the surface temperature remains constant (after a brief period due to the finite heat capacity of the metal ribbon employed in the studies) while the energy flux into the propellant decreases with time. As a matter of fact the surface temperature gradient may become negative if the heat release rate in the condensed phase exceeds the heat input from the ribbon source. For the theoretical analysis of ignition by radiative* and conductive heat transfer the one-demensional heat conduction equation with exothermic heat release in the condensed phase reads:

$$T_t(x,t) = KT_{xx}(x,t) + S \exp(-E/RT) \qquad (1)$$

where the first term on the rhs of the equation represents the contribution due to heat conduction and the second, due to exothermic chemical reaction. The following boundary conditions apply for radiative heat transfer:

$$-KT_x(0,t) = I/c\rho \qquad (2)$$

$$T(x_m,t) = 0 \qquad (3)$$

$$T(x,0) = T \qquad (4)$$

---

*Equation (1) represents a good approximation for a body of finite absorptivity when the parameters $K\alpha^2 t > 10$, a requirement satisfied under our experimental conditions.[7]

For conductive heat transfer the boundary condition represented by Eq. (2) is replaced by

$$T(0,t) = \begin{cases} T_0 + t(T_1-T_0)/t^*, & t < t^* \quad (5) \\ T_1 \quad , & t > t^* \quad (6) \end{cases}$$

while Eqs. (3) and (4) still apply.

For the case of conductive heat transfer the finite time t^* required for the ribbon to attain a steady-state temperature T_1 was taken into account as expressed by Eq. (5). In addition, the cold end of the propellant at $x = x_m$ was considered to be insulated as specified by Eq. (7). The magnitude of x_m was chosen large enough so that the temperature at that point did not rise by more than a few degrees above the initial temperature. For the time periods of interest to the problem the solutions obtained are effectively the same as those for a semi-infinite slab. Because of the exponential nature of the heat release term associated with exothermic reaction ($\dot{q}/c\rho$), Eq. (1) was solved numerically.

In the mathematical analysis the criterion for ignition was chosen such that, in the case of radiation, the thermal runaway occurs at a surface temperature which exceeds by 10 percent the temperature to be expected in the absence of exothermic reaction.[4] In the case of conduction the ignition time was defined as that interval required for the temperature gradient at the surface to attain a value of zero. The latter criterion is based on theoretical considerations indicating that in the temperature range of concern to our ignition experiments the approach to a zero gradient at the surface is the result of a significant contribution of heterogeneous exothermic reactions in the condensed phase.

The differential equation (Eq. 1) was solved numerically using a modified Crank-Nicholson technique. The heat release rates employed

were those measured by means of adiabatic studies[8] for the propellants under investigation. The kinetic data are summarized in Table 2. In addition, temperature-averaged values were employed for the thermal diffusivity, specific heat, and density, on the basis of the experimental results presented in reference 4.

The ignition experiments for propellant B with radiation as an energy source demonstrate the critical contribution of heterogeneous reactions to the ignition process. As can be seen from the data presented in Fig. 1 the experimental results show general agreement with the theoretical calculations based on a thermal runaway in the condensed phase as a trigger for ignition of a propellant containing AP and binder. The same type of ignition behavior had previously been observed for a propellant composed of AP and copper chromite in the absence of binder.[4]

For propellant ignition by conductive heat transfer the results obtained for two propellants are shown in Figs. 2 and 3. Again a comparison with the theoretical curves confirms the hypothesis of distributed heat sources near the surface of the propellant as the trigger for ignition. The experimental data shown refer to the steady-state maximum temperatures of the niobium ribbon rather than average temperatures. (The data employing average temperature fall to the left of the theoretical curves).

IV. DISCUSSION

As was mentioned previously, the physical characteristics of the ignition stimuli used in our studies show marked differences. However, since propellants of the same composition were employed it is of interest to see whether certain physical or chemical conditions are common to both ignition modes, radiative and conductive. For this examination we may consider the following parameters: ignition time, ignition temperature, and total energy stored at time of ignition.

The curves shown in Fig. 4 clearly demonstrate the marked differences in propellant surface temperature associated with radiative and

conductive heat transfer. It can be seen that for a specified ignition time (t_i) the surface temperature at ignition by conduction is well below that at ignition by radiation, except in the case of conductive heat transfer with a long rise time for the heating element (i.e., high inherent heat capacity of the energy source). At short ignition times corresponding to high energy fluxes, the differences in surface temperature associated with the two ignition modes become smaller. In part this behavior reflects the fact that in the radiative case the surface temperature is rising continuously from the initial value (room temperature), while in the case of conduction the surface temperature is fixed at a high value and is maintained at that level until ignition occurs.

Next it is of interest to inquire into the total amount of energy present in the propellant at ignition. This energy term per unit area represents the sum of the energy introduced by radiation or conduction at the surface of the propellant (E_1) and the energy generated by distributed exothermic surface-coupled reactions (E_2):

$$E = \int_0^t - \lambda T_x(0,t)\ dt + \int_0^t c\rho\left[\int_0^\infty S \exp(-E/RT)(x,t)\ dx\right] dt$$

The results of these calculations indicate that for the same ignition times the energy surface density in a given propellant is considerably higher under conditions of conductive heat transfer than under those of radiative heat transfer (Fig. 5). It is concluded therefore that for radiative ignition within a specified time interval the surface temperature is higher and the energy stored less than in the case of conductive ignition. It is apparent therefore that the propellant response to the two ignition stimuli explored in this study is entirely different.

ACKNOWLEDGMENTS

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Nomenclature

c = specific heat, cal/g-deg

E = activation energy, cal/mole

I = radiation flux, cal/cm^2-sec

K = thermal diffusivity, cm^2/sec

$\dot{q}$ = heat-release rate, cal/cm^3-sec

S = pre-exponential heat-release term, deg/sec

t = time, sec

T = temperature, ^{0}K

x = distance coordinate, cm

λ = thermal conductivity, cal/cm-sec-deg

ρ = density, g/cm^3

Subscripts

t = derivative with respect to t

x = derivative with respect to x

0 = conditions at time zero

Superscript

$*$ = conditions at specified time

Table I

Propellant Composition

Material	A (CTPB)	B (Butarez)	C (PU-174)
	Weight Percent		
Ammonium perchlorate[a]	75.00	75.00	80.00
Polybutadiene (carboxy-terminated)[b]	20.24	19.44	--
Tris[1-(2-methyl)-aziridinyl] phosphine oxide	0.40	0.38	--
Triglycidyl-paraaminophenol	0.11	0.11	--
Dioctyladipate	4.24	4.07	-
Magnetite	--	1.00	--
Toluene diisocyanate	--	---	2.44
Polypropylene glycol	--	--	17.00
Trimethylol	--	--	0.40
Triethanolamine	--	--	0.16

[a]From American Potash Co., Trona, California, technical grade.

[b]From Phillips Petroleum Co., Bartlesville, Oklahoma.

Table 2

Kinetics of Heat Release

Propellant	dT/dt, deg/sec
A	$10^{12.9}$ exp (-33,000/RT)
B[a]	$10^{12.9}$ exp (-33,000/RT)
C[b]	$10^{12.77}$ exp (-35,500/RT)

[a]The small amount of magnetite in propellant B has little effect on the kinetics of heat release relative to that observed in propellant A.

[b]Results from Reference 9.

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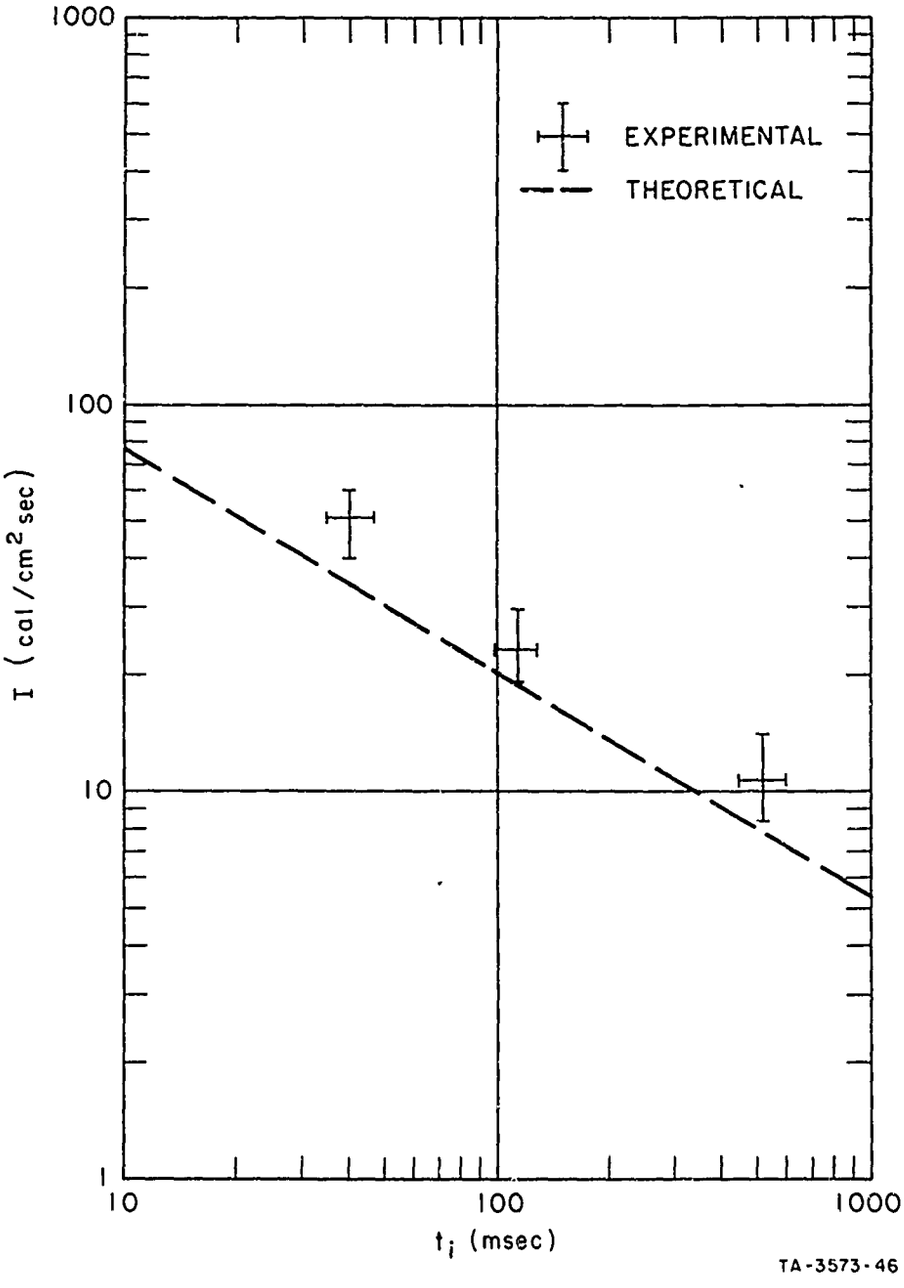
1000
100
10
1
10
100
1000
I (cal/cm² sec)
t_i (msec)
EXPERIMENTAL
THEORETICAL
TA-3573-46

FIG. 1

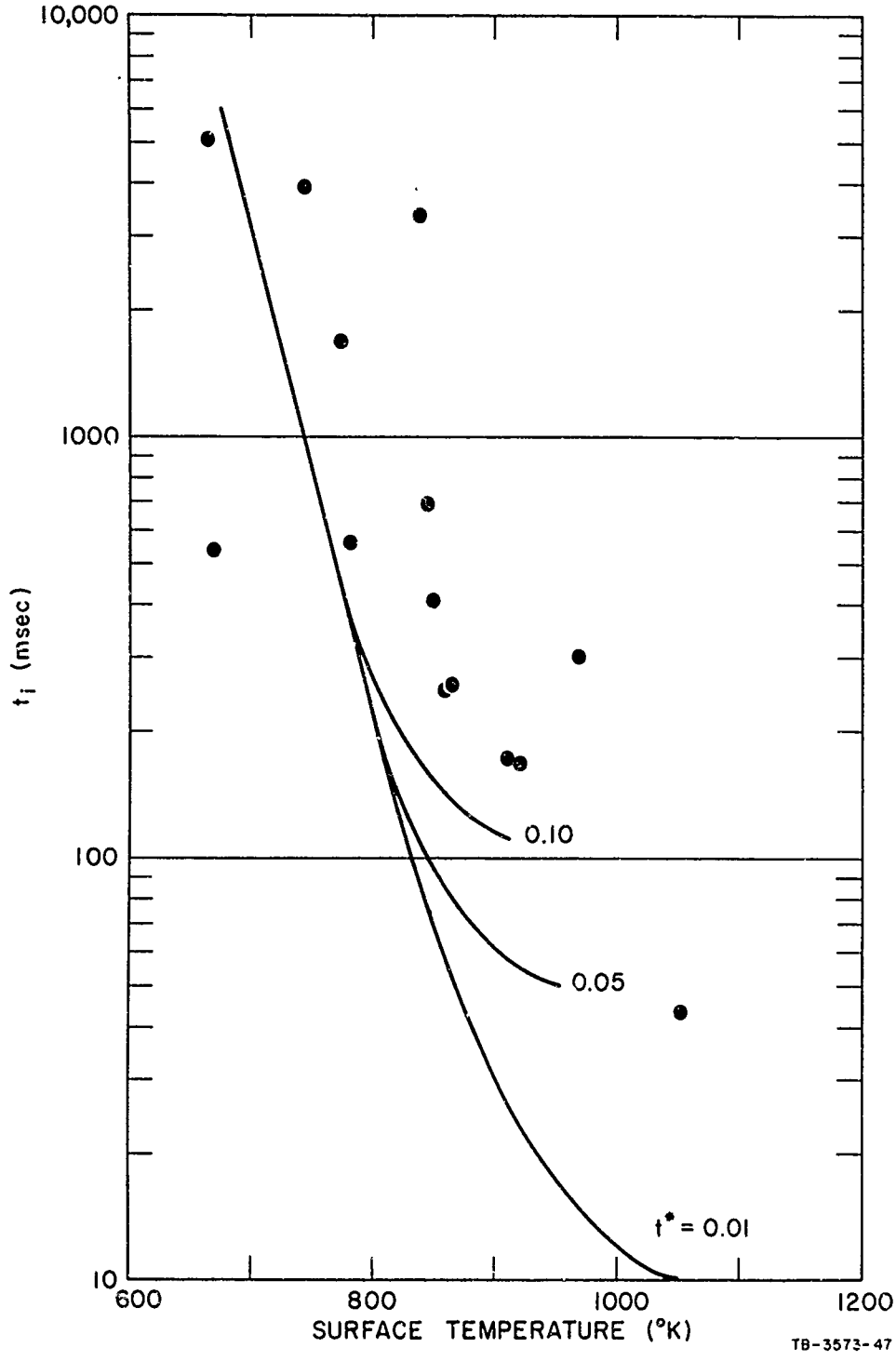
10,000
1000
100
10
t_i (msec)
0.10
0.05
$t^* = 0.01$
600
800
1000
1200
SURFACE TEMPERATURE (°K)
TB-3573-47

FIG. 2

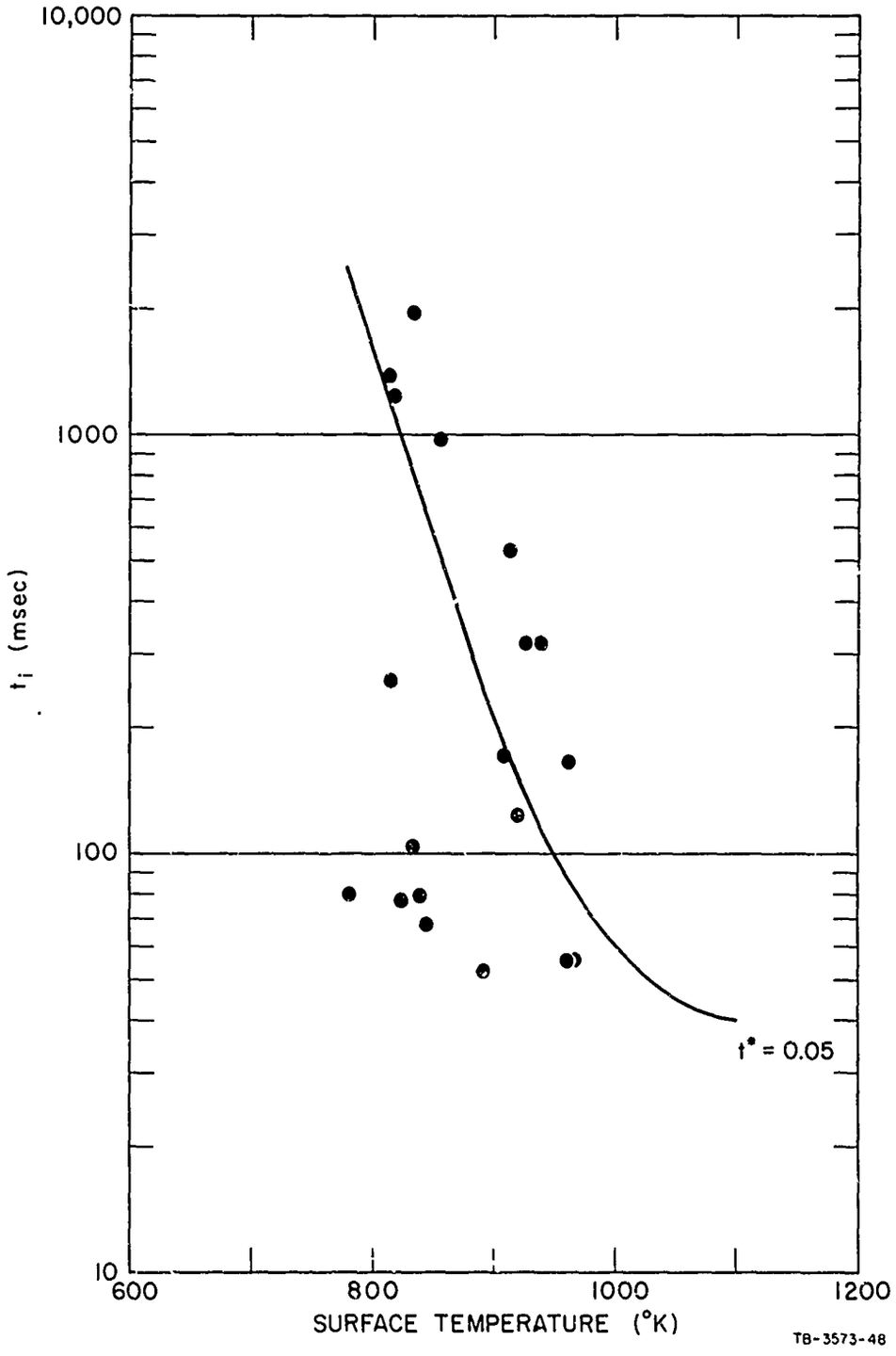
10,000
1000
100
10
t_i (msec)
600
800
1000
1200
SURFACE TEMPERATURE (°K)
$t^* = 0.05$
TB-3573-48

FIG. 3

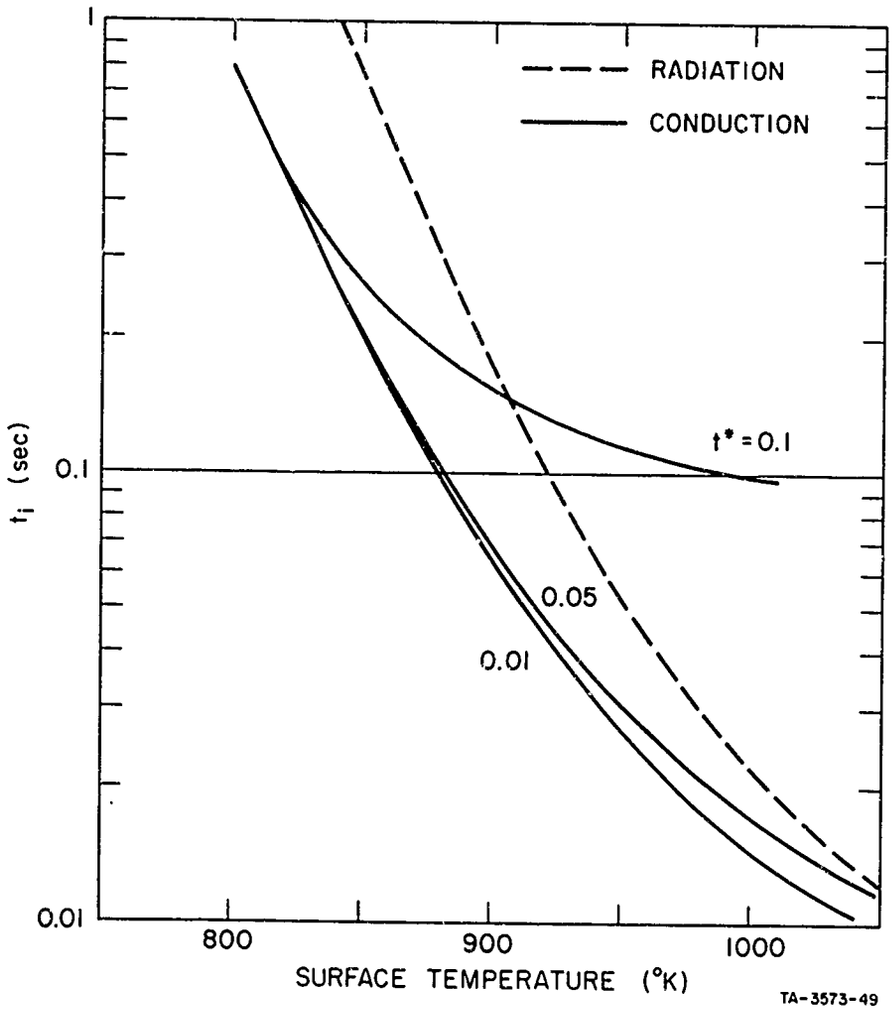
RADIATION
CONDUCTION
t* = 0.1
0.05
0.01
1
0.1
0.01
t_i (sec)
800
900
1000
SURFACE TEMPERATURE (°K)
TA-3573-49

FIG. 4

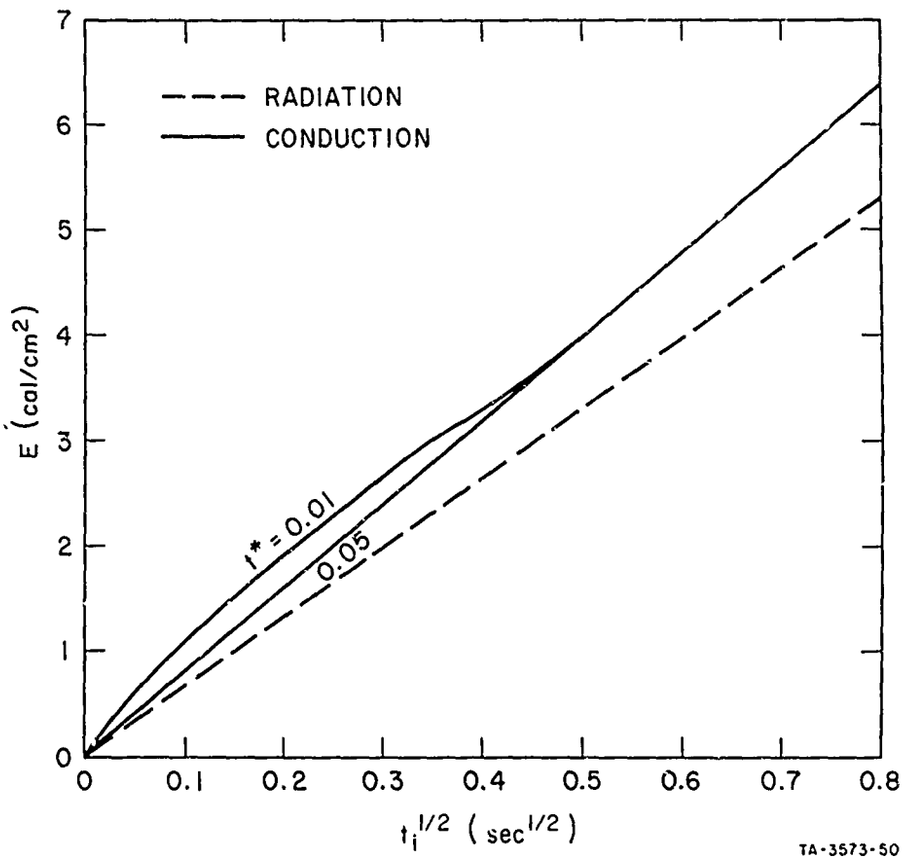
RADIATION
CONDUCTION
t* = 0.01
0.05
E (cal/cm²)
t_i^1/2 (sec^1/2)
0
1
2
3
4
5
6
7
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
TA-3573-50

FIG. 5

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13. ABSTRACT

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT